AD

Technical Report ARWSB-TR-12007

NEW PVD TECHNOLOGIES FOR NEW ORDNANCE COATINGS

S.L. Lee, R. Wei, J. Lin, R. Chistyakov, D. Schmidt, M. Cipollo,
F. Yee, and M. Todaro

April 2012

ARMAMENT RESEARCH, DEVELOPMENT AND ENGINEERING CENTER
Weapons & Software Engineering Center
Benét Laboratories

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
16-04-2012

2. REPORT TYPE
Technical Report

3. DATES COVERED *(From - To)*
September 2008-September 2010

4. TITLE AND SUBTITLE
New PVD Technologies for New Ordnance Coatings.

5a. CONTRACT NUMBER
W15QKN-09-P-0348

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
S.L. Lee, R. Wei, J. Lin, R. Chistyakov, D. Schmidt, M. Cipollo, F. Yee, and M. Todaro

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
U.S. Army ARDEC
Benet Laboratories, RDAR-WSB
Watervliet, NY 12189-4000

8. PERFORMING ORGANIZATION REPORT NUMBER
ARWSB-TR-12007

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army ARDEC
Benet Laboratories, RDAR-WSB
Watervliet, NY 12189-4000

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSORING/MONITORING AGENCY REPORT NUMBER

12. DISTRIBUTION AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited (October 2011).

13. SUPPLEMENTARY NOTES
Prepared in cooperation with the Colorado School of Mines and Southwest Research Institute.

14. ABSTRACT
This report summarizes a two-year effort on an EQBRD project. The objective was to research and develop new plasma enhanced physical vapor deposition technologies for deposition of pollution-free coatings for protection of armament components to extend cycle life. In this paper, technology research and development included: 1) Physical Vapor Deposition processes including plasma enhanced magnetron with external ion source, High Power Impulse Magnetron Sputtering (HIPIMS), and Modulated Pulsed Power (MPP); 2) Innovations of the HIPIMS and MPP processes based on the physics of Ionized Physical Vapor Deposition; 3) The plasma ion and mass characteristics using a Tantalum and a Chrome target; 4) Deposition of Ta coatings and reactive deposition of CrN; 5) Deposition parameters affecting film nucleation and growth properties; 6) Coatings characterization.

15. SUBJECT TERMS
Electroplated high contraction chromium (HC Cr) coatings; Physical Vapor Deposition (PVD); High Power Impulse Magnetron Sputtering (HIPIMS); Modulated Pulsed Power (MPP); Tantalum; Chrome; Ta coatings; CrN; coating characterization.

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**	U/U	29	Susan Macksey
U/U	U/U	U/U			**19b. TELEPONE NUMBER (*Include area code*)** 518-266-5613

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI-Std Z39-18

INSTRUCTIONS FOR COMPLETING SF 298

1. REPORT DATE. Full publication date, including day, month, if available. Must cite at lest the year and be Year 2000 compliant, e.g., 30-06-1998; xx-08-1998; xx-xx-1998.

2. REPORT TYPE. State the type of report, such as final, technical, interim, memorandum, master's thesis, progress, quarterly, research, special, group study, etc.

3. DATES COVERED. Indicate the time during which the work was performed and the report was written, e.g., Jun 1997 - Jun 1998; 1-10 Jun 1996; May - Nov 1998; Nov 1998.

4. TITLE. Enter title and subtitle with volume number and part number, if applicable. On classified documents, enter the title classification in parentheses.

5a. CONTRACT NUMBER. Enter all contract numbers as they appear in the report, e.g. F33615-86-C-5169.

5b. GRANT NUMBER. Enter all grant numbers as they appear in the report, e.g. 1F665702D1257.

5c. PROGRAM ELEMENT NUMBER. Enter all program element numbers as they appear in the report, e.g. AFOSR-82-1234.

5d. PROJECT NUMBER. Enter al project numbers as they appear in the report, e.g. 1F665702D1257; ILIR.

5e. TASK NUMBER. Enter all task numbers as they appear in the report, e.g. 05; RF0330201; T4112.

5f. WORK UNIT NUMBER. Enter all work unit numbers as they appear in the report, e.g. 001; AFAPL30480105.

6. AUTHOR(S). Enter name(s) of person(s) responsible for writing the report, performing the research, or credited with the content of the report. The form of entry is the last name, first name, middle initial, and additional qualifiers separated by commas, e.g. Smith, Richard, Jr.

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES). Self-explanatory.

8. PERFORMING ORGANIZATION REPORT NUMBER. Enter all unique alphanumeric report numbers assigned by the performing organization, e.g. BRL-1234; AFWL-TR-85-4017-Vol-21-PT-2.

9. SPONSORING/MONITORS AGENCY NAME(S) AND ADDRESS(ES). Enter the name and address of the organization(s) financially responsible for and monitoring the work.

10. SPONSOR/MONITOR'S ACRONYM(S). Enter, if available, e.g. BRL, ARDEC, NADC.

11. SPONSOR/MONITOR'S REPORT NUMBER(S). Enter report number as assigned by the sponsoring/ monitoring agency, if available, e.g. BRL-TR-829; -215.

12. DISTRIBUTION/AVAILABILITY STATEMENT. Use agency-mandated availability statements to indicate the public availability or distribution limitations of the report. If additional limitations/restrictions or special markings are indicated, follow agency authorization procedures, e.g. RD/FRD, PROPIN, ITAR, etc. Include copyright information.

13. SUPPLEMENTARY NOTES. Enter information not included elsewhere such as: prepared in cooperation with; translation of; report supersedes; old edition number, etc.

14. ABSTRACT. A brief (approximately 200 words) factual summary of the most significant information.

15. SUBJECT TERMS. Key words or phrases identifying major concepts in the report.

16. SECURITY CLASSIFICATION. Enter security classification in accordance with security classification regulations, e.g. U, C, S, etc. If this form contains classified information, stamp classification level on the top and bottom of this page.

17. LIMITATION OF ABSTRACT. This block must be completed to assign a distribution limitation to the abstract. Enter UU (Unclassified Unlimited) or SAR (Same as Report). An entry in this block is necessary if the abstract is to be limited.

Table of Contents

A. FY09-10 EQBRD Proposal:

Title: New PVD Technologies for New Ordnance Coatings

Organization:

Dr. Sabrina Lee
US Army ARDEC-Benet Labs
Watervliet, NY 12189-4050
518-266-5503 (Commercial); DSN 374-5503; 518-266-4661 (Fax)

Email- Sabrina.l.lee@us.army.mil

1) Problem Statement:

Electroplated Cr is widely used in industry and in the military to improve service life of weapon systems parts. Current tri-service weapon systems production process uses NaOH in the pre-cleaning of parts and electro-polishing in concentrated H_2SO_4 and H_3PO_4 acids bath prior to deposition. It then uses electroplated Cr plating process to deposit coatings on the bore of barrels for high temperature wear and erosion protection, and on weapon systems parts, such as split rings, spindles, rods to protect against wear and corrosion. The pre-deposition cleaning, electro-polishing, and Cr electroplating process produces aqueous toxic wastes, detrimental to the environment and to public health. The pre-production chemicals and acids are hazardous and hexavalent Cr is a known carcinogen. Significant annual expenditures are necessary to treat and to dispose these aqueous toxic chemical pollutants.

In addition, new weapon systems use more erosive propellants, use hotter ammunition and require higher firing power. Electroplated Cr has extensive as-deposited and firing-induced cracks, which allow hot propellant gases to penetrate to erode the gun bore. Life cycle requirements for large cal such as the 120mm M256 and XM360 weapon systems cannot be met with current Cr electroplating process. In addition, currently chamber section of M776 is Cr coatings, but rifled section of production 155mm M776 is not Cr coated. The realized cycle life for the M776 is only ~900 EFC, while minimum 1500 EFC performance is required, well shy of the fatigue life of 2650 EFC. Production Cr electroplating process is being considered to coat the M776 for improved cycle life. This may provide a temporary partial solution, since the electroplated Cr environmental problem remains and cycle life performance is still limited.

Objective: In this proposal, research and development in new PVD (physical vapor deposition) technologies, based on ionized PVD, are being explored for ordnance applications in eliminating pollutants and increasing cycle life. Magnetron sputter clean and deposition can eliminate the necessity of pre-deposition chemicals, electropolishing in acid bath and Cr electroplating processes. This proposal targets 155mm XM777 and XM324 parts, such as split ring, spindle,

and the rifled bore. Technology developed in this proposal has wide range of applications since the tri-services deposit electroplated Cr coatings on numerous ordnance parts.

2) AERTA Requirements:

The proposal meets the following requirements listed in AERTA (Army Environment Requirements and Technology Assessment):

1) PP-2-02-03 'Heavy Metal Reduction in Surface Finishing Processes'
2) PP-3-02-04 'Compliant Ordnance Lifecycle for Readiness of Transformation Forces'.
3) PP-4-02-03 'Alternative Products in Cleaning and Degreasing Processes'.

3) Impact Statement:

If the proposal is not funded, the cleaning chemicals and Cr electroplating problems cannot be resolved. Current technology will incur violations to the Army environmental regulatory requirements. In addition, this will have an impact on the environment and public health to meet AERTA requirements. The will also cause impact on the readiness of the Armed Forces due to the safety, durability, and life cycle issues of Cr plated weapon systems for our soldiers.

4) Project Description:

- Technical Objective: To research and develop new physical vapor deposition technologies via ionized PVD process for ordnance coatings applications for pollution-prevention and cycle life improvement.

.

- Technical Approach:

Ionized PVD magnetron sputtering process differs from conventional PVD in that high percentage of target ions instead of neutrals are used for film nucleation and growth. The physics of charge exchanges and other cross sections associated with ionized PVD is different from momentum transfer in conventional PVD magnetron sputtering, resulting in expected improvement of film quality. New high power impulse magnetron power supply is needed to implement the new process. Ion-surface interactions, film growth using energetic high flux metal ions, and effects of high flux energetic ions will be studied. Engineered interface, growth morphology, and residual stress management will be explored to improve coatings quality and performance.

Year	Tasks
2009	1) Planning and contracting. 2) Installation of HIPIMS-MPP power supplies. 3) Parametric study of effects of degree of ionization, power level, biasing, Ar gas pressure. 4) Interface engineering and film growth morphology management to optimize coatings.
2010	1) Coating deposition on 120mm and 155mm test samples. 2) Analytical photomicrograph, XRD, SEM for phase, stress, morphology, microstructure. 3) Groove test, pulsed laser heating test. 4) Reporting-Publication.

- Milestones:

Task Milestones	FY09 1Q	FY09 2Q	FY09 3Q	FY09 4Q	FY10 1Q	FY10 2Q	FY10 3Q	FY10 4Q
Project Funding/ Planning/ Contracting	X							
New power supply Implement/toning	X	X	X					
New PVD process development		X	X	X	X			
Deposition on 120mm and 155mm test samples			X	X	X	X		

Analytical and adhesion characterization						X	X	X

- **Research Team**:

Personnel	Office Symbol	Phone Number
Dr. Sabrina Lee (PI)	AMSRD-AAR-WSB-LC	518-266-5503
Mick Cipollo	AMSTA-AAR-WSB-LB	518-266-5050
Fang Yee	AMSTA-AAR-WSB-LC	518-266-5045

- **Cooperative Research and Development**

Personnel	Organization	Phone Number
Dr. Bill Sproul	Colorado School of Mines	760-295-5787
Dr. Ronghua Wei	Southwest Research Institute	210-522-5204

- **Cost Estimate:**

Year	In-House Labor	Material	Travel	Contract	Total
2009	$70k	$10k	$5k	$15k	$100k
2010	$115k	$10k	$5k	$20k	$150k

Leveraging R-TOC funding; PI was Dr. S.L. Lee: 'Plasma Enhanced Cylindrical Magnetron':

Year	R-TOC Funding
2008-2009	$1.402 M (In-House Labor $852K, Equipment $100K, Contract Labor $450K)

5) Specific Expectations:
Innovations of the new process include the following: 1) dense films with no inter-grain voids; 2) Graded interface, e.g. Ta/Fe, Cr/Fe for improved adhesion; 3) can uniformly coat irregular shaped geometry. We can thus expect the new process to produce pollution-free dense and adhesive coatings on irregular geometry after the process is properly transitioned, such as the 155 rifled bore and spindles.

6) Transition Plan:
The technology, once developed, can be applied to numerous military and industrial systems by depositing metallic and nano-composite coatings targeting specific desired properties. There is no more need of pre-deposition cleaning chemicals, acid cleaning bath, or toxic Cr electroplating pollutants. Several 6.2/6.3 research topics can result from the current research for ordnance coatings and service life improvement.

B. Research Team, Funding, Cost:
Project Management & Technical Lead: Dr. Sabrina Lee
Cooperative R&D: Dr. Ronghua Wei (SWRI), Dr. B. Sproul (Colorado School Mines)
ARDEC Team: D. Schmidt, Mick Cipollo, Fang Yee, M. Todaro

Year	Funding Received	In-House Labor	Material	Travel	Contract	Actual Cost
2009	100k	$85k	$10k	$5k		$100k
2010	150k	$115k	$10k	$5k	$20k*	$150k

* Southwest Research Institute, Contract No. W15QKN-09-P-0348, awarded 23 Sept 2009, partial contribution $20k from EQBRD project fund.

C. Technical Accomplishments

Abstract

This report is to summarize a two-year (FY09-FY10) effort for an EQBRD project entitled ‘New Physical Vapor Deposition Technologies for New Ordnance Coatings’. The objective of the project was to research and develop new plasma enhanced physical vapor deposition technologies for deposition of pollution-free coatings for protection of armament components to extend cycle life. Electroplated high contraction chromium (HC Cr) coatings have been used for decades to extend service life of armament components. It is deposited on the external surfaces of ordnance and on the interior surfaces of cylinders against wear, erosion, and corrosion. In this paper, technology research and development included: 1) Physical Vapor Deposition (PVD) processes including plasma enhanced magnetron with external ion source (PEMS), High Power Impulse Magnetron Sputtering (HIPIMS), and Modulated Pulsed Power (MPP); 2) Innovations of the HIPIMS and MPP processes based on the physics of Ionized Physical Vapor Deposition (I-PVD); 3) The plasma ion and mass characteristics using a Tantalum and a Chrome target; 4) Deposition of Ta coatings and reactive deposition of CrN; 5) Deposition parameters affecting film nucleation and growth properties; 6) Coatings characterization. The results demonstrated the potential that the new technologies offer alternative coatings to replace HC Cr for ordnance wear-erosion-corrosion applications.

1. Introduction

The objective of the EQBRD project is to research and develop new plasma enhanced Physical Vapor Deposition (PVD) technologies, including Plasma Enhanced Magnetron Sputtering (PEMS), High Power Impulse Magnetron Sputtering (HIPIMS), and Modulated Pulsed Power (MPP). This report summarizes the plasma generation, plasma characteristics, effects of increased ion bombardment, effects of deposition parameters on the deposition of Ta and CrN coatings. Since PEMS technology produces high intensity plasma, and HIPIMS and MPP technologies generate high ionization and high concentrations of target metal plasma, ion-surface interactions, film growth using energetic high flux metal ions, effect of high flux energetic ions on growth morphology, need for residual stress management and engineered interface will be explored.

2. Physical Vapor Deposition Processes

Physical vapor deposition (PVD) is used to deposit coatings and thin films by the condensation of the vaporized form of materials via physical processes, such as high temperature evaporation or plasma sputter bombardment. PVD processes are gaining increasing importance worldwide due the broad based applications into engineering and commercial systems and products. Magnetron

sputtering can be operated at high power levels to achieve high plasma densities. For conventional DC magnetron sputtering, the maximum power is limited by the thermal load on the target provided by bombardment of the positive ions. To avoid this limitation, the power may be applied in pulses. By decreasing the duty cycle (on-time divided by the cycle-time), a corresponding increase in power during the on-time pulses can be achieved. In the high power impulse magnetron sputtering (HIPIMS), the power is extremely high at > 1000 W/cm^2 to obtain highly ionized metal plasma. In Fig. 1, DCMS and HIPIMS discharges are compared for a Cr target following the exponent $I_d = k_d V_d^n$ law [1]; for conventional magnetron discharge, n = 5…10, for HIPIMS, n=1. The HIPIMS and the MPP processes, as described in the following sections, have, in recent years, revolutionized the PVD magnetron sputter coating process. Due to the high pulsed power, the metallic species sputtered from the metal target achieved high degree of ionization to produce dense quality films at relatively low temperature.

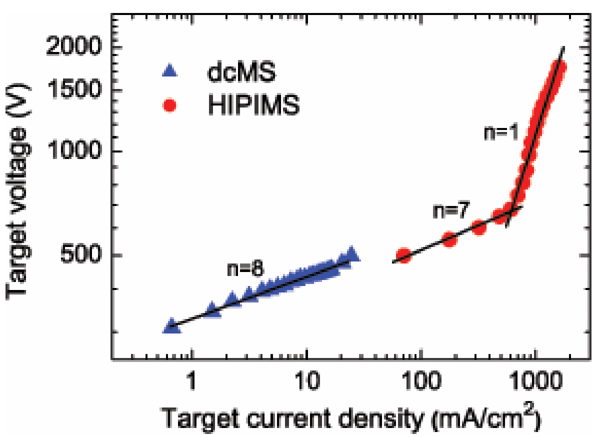


Fig. 1 Comparison of DCMS and HIPIMS discharge I-V Characteristics: The exponent n of the power law $I_d = k_d V_d^n$ is indicated. The target is Cr and the Ar pressure is 3 mTorr; from Ehiasarian et al [1].

2a) Direct Current Magnetron Sputtering (DCMS): In DCMS, the magnetron is driven by a DC power supply, and target neutrals are used to deposit coatings. DCMS is the conventional coating and thin film deposition process. The process can generally be run with or without substrate bias. DCMS generally generates plasma with low ionization. DCMS does not generate droplets, which are clusters and macro-particles, often observed in cathode arc deposited coatings.

2b) Plasma Enhanced Magnetron Sputtering (PEMS): In the new coatings innovation using PEMS, external ion sources are used to provide more abundant ions for improved plasma characteristics. For instance, a thermionic filament-generated plasma or RF-generated plasma can be used to increase ion current. The additional ion bombardments can be used both for substrate cleaning and for the deposition of dense quality coatings for potential ordnance applications. While DCMS generated local plasma produce ion current of 0.2mA/cm2 measured at the substrate, external ion source can generate global plasma. The combined magnetron plus global plasma can produce an ion current of 4.9mA/cm^2, a 25 fold increase at the surface of the

substrate. The increased ion bombardment can produce Improvement of film topography and microstructure. In Fig. 2, example Cr films were deposited on A723 steel at discharge currents of 0, 5, 10, 20 Amp. The data demonstrated that increased ion bombardment at various discharge current can produce films with less columnar microstructure, more smooth surfaces, and higher hardness [2]. The enhanced plasma in the PEMS process was used to more thoroughly clean the substrate and to deposit thick Ta coatings on curved barrel test samples with excellent structural characteristics and vented erosion simulator firing test of over 100 hot rounds, with excellent adhesion, no cracking and no delamination were observed [2, 3].

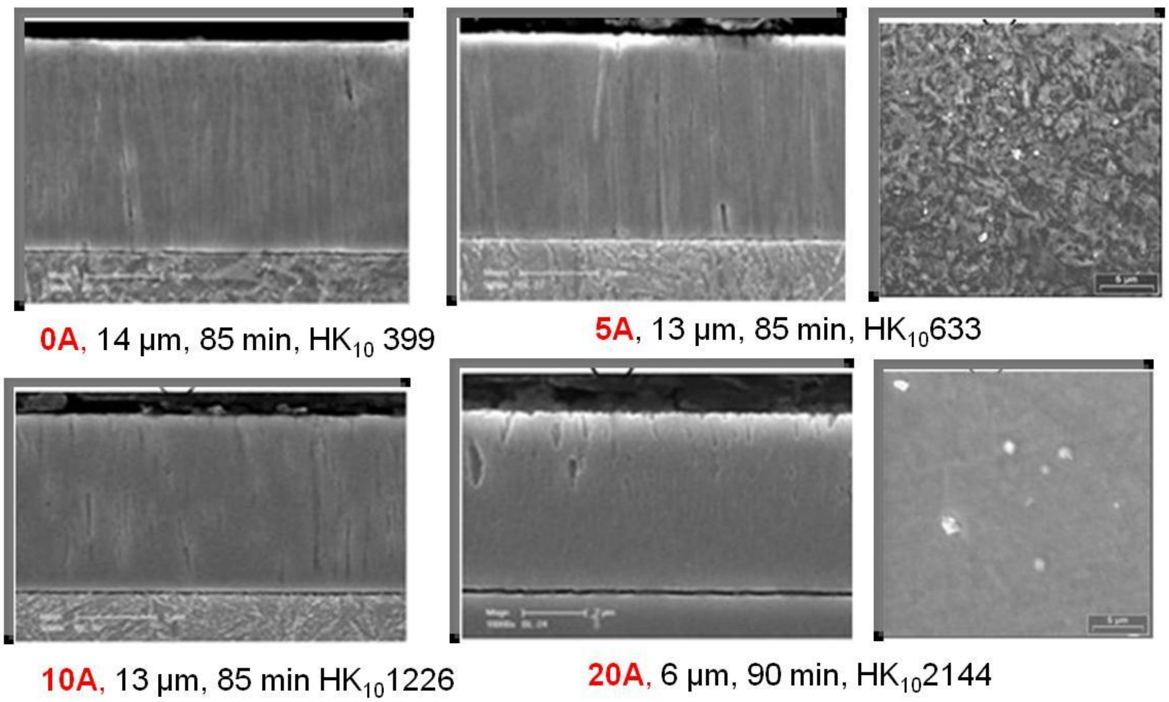


Fig. 2 Topography and microstructure of Ta films deposited at increasing ion bombardment, indicated by increased discharge current at 0, 5, 10, 20 A; with corresponding increased film hardness, using PEMS technology [2].

2c) High Power Impulse Magnetron Sputtering (HIPIMS): When a HIPIMS power supply is used, the high power ionizes the metal target and generates high intensity, high ionization plasma [4-6]. Metal ions in the plasma can be used to clean the substrate. Diffusion bonding of implanted ions can improve coatings adhesion; and the abundant ions can deposit near full dense coatings on desired substrates with improved coverage due to ion-surface interaction. Typically, the pulse width is short, up to 250 μs. The pulse voltage waveform is unregulated and hence the pulse current is determined by the total impedance of the magnetron circuitry. In general, HIPIMS generates peak power (1-3 kW/cm^2), 1000 times greater than conventional DCMS; high

power pulses of short duration (100-250 µs for HIPIMS, longer for MPP); and low duty cycle (1-10% for HIPIMS, but up to 25% for MPP processes).

2d) **Modulated Pulse Power (MPP)** is an enhancement to the HIPIMS technology using a MPP plasma generator power supply. The process utilizes a longer DC pulse (1 ms) than that used in HIPIMS. In addition, the pulsed voltage waveform is modulated with a specific profile. At the beginning of the pulse, a low voltage is used to ignite the plasma. The voltage is then increased, such that the current and hence the power are increased. In this way, arcing is reduced while high power sputtering is achieved. HIPIMS and MPP are very similar technologies; they are treated as HIPIMS-MPP in this work. In the Modulated Pulse Power the power density is ~ 0.1-1.0 kW/cm^2, multi-step DC negative voltage pulse takes up several steps, shown in Figure 3: 1) ignition of low power discharge; 2) low power discharge; 3) transient stage from low power discharge to high power discharge; 4) high power discharge; thus enabling a long, stable, and high power pulse discharge pulses widths of > 200 µsec up to 3 msec. to increase deposition rate [7]. Similar wave forms are used in the deposition of Ta and CrN films in this report [7].

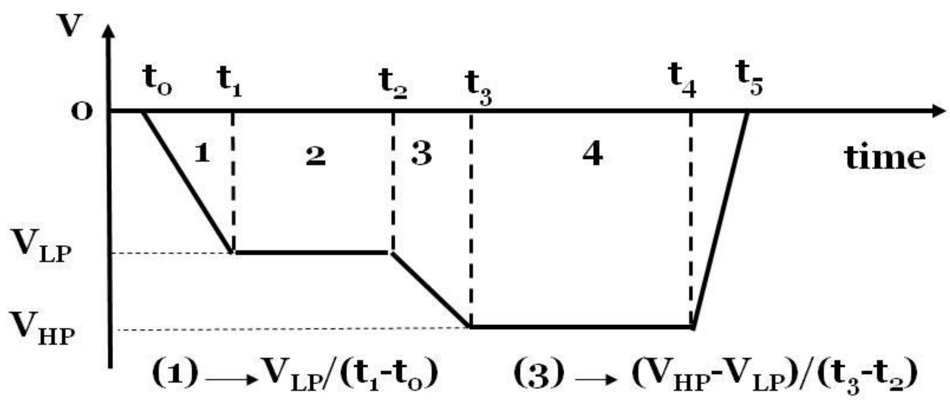


Fig. 3 Characteristics of Modulated Pulsed Power (MPP) wave form [7].

3. Material Selection

Tantalum, in its common bulk body centered cubic (body-center-cubic) alpha Ta form, is highly refractory (with melting temperature of 2996ºC vs. 1860ºC for chromium) and has a relatively low thermal conductivity (57 W/mºC vs. 91 W/mºC for Cr @20ºC). In addition, tantalum is chemically resistant to corrosive propellant gases and the bcc phase is much more ductile than electrodeposited high contractile (HC) chromium, making it far less susceptible to crack formation and subsequent coating failure in barrel applications. Tantalum is also environmental friendly with no effects on human health. Ta also forms in hard and brittle meta-stable tetragonal beta Ta form. Beta Ta is believed to transform into alpha Ta at 750ºC. However, it was found that highly textured beta Ta can transform into alpha Ta at lower temperature [8]. Ta is being studied for potential replacement for HC Cr for high temperature wear and erosion.

Chrome nitride generally forms in face-centered-cubic (face-center-cubic CrN, lattice parameter 4.14 angstroms) and hexagonal Cr_2N crystalline structures. It can easily be deposited using reactive magnetron sputtering technologies. Chromium nitride has high hardness, good modulus of elasticity, low coefficient of friction, and excellent properties against wear, corrosion, oxidation, abrasion. It is being studied to coat surfaces of armament components operating at lower temperatures compared to the cannon bore.

4. Experimental Instrumentation and Method:

4a) Benet Design of Experiment (DOE) cylindrical magnetron sputtering deposition system was previously set up to deposit on the bore of gun barrels with a flash electroplated Cr interface layer using DCMS without biasing. Under the current investigation, substrate biasing capability was implemented using an anode ring design [9], and a Zpulser Axia-100 MPP plasma generator power supply (100 kW peak power) was installed to power the system, as shown in Fig. 4a. Typical wave forms used for Benet plasma enhanced cylindrical magnetron system are shown in Fig.4b, giving the discharge voltage, discharge current, and the substrate ion current.

4b) A plasma-enhanced cylindrical magnetron system, which can be powered with a either a DCMS or a HIPIMS magnetron power supply at Southwest Research Institute (SWRI) is shown in Fig.4b. SWRI system used two magnetron designs: rectangular and ring magnets, both showed enhanced plasma intensity.

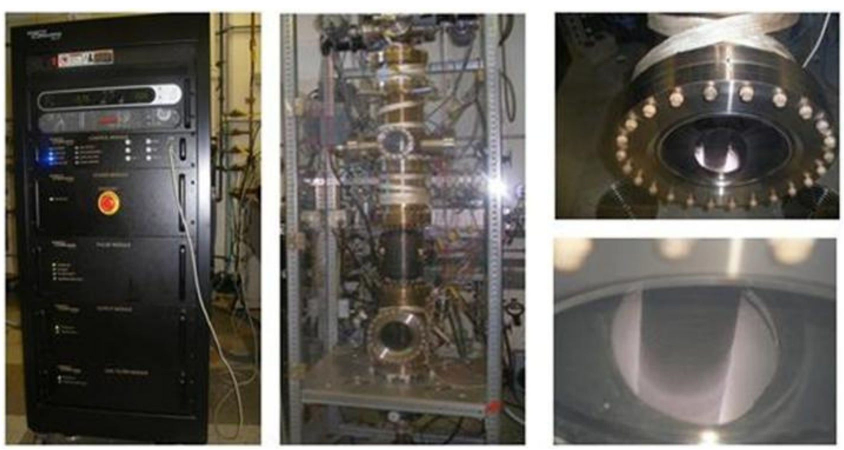


Fig. 4a Benet Plasma Enhanced DOE system: Zpulser MPP power supply assembly (left); DOE plasma enhanced deposition platform to coat 120mm cylinder (middle); enhanced plasma using a Tantalum target (right).

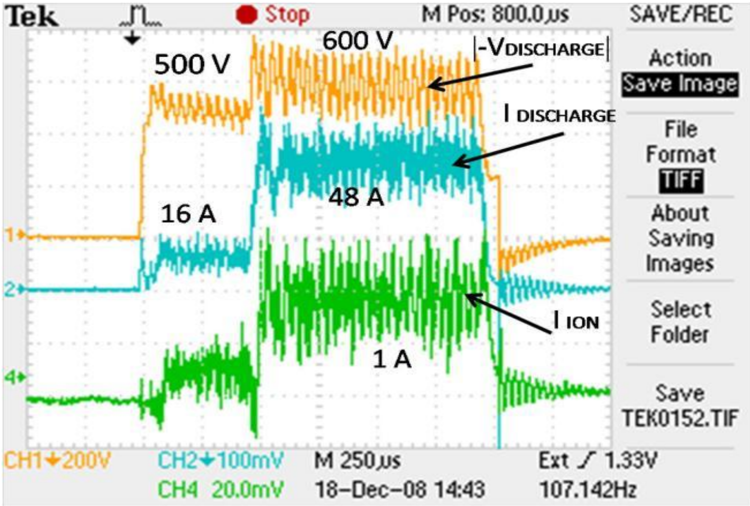


Fig. 4b MPP Waveform characteristics showing: 1) discharge voltage (top line); 2) discharge current (middle), and 3) substrate ion current (bottom) using a Zpulser MPP plasma generator power supply at Benet.

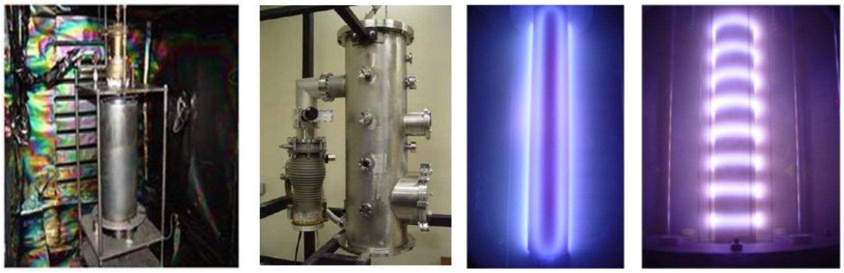


Fig. 4c Biased DCMS and HIPIMS cylindrical sputter deposition systems at Southwest Research Institute, showing two target designs- left used rectangular magnet, right used ring magnet.

4c) In order to study the effect of deposition parameters, such as substrate bias and argon gas pressure, on Ta properties, two planar magnetron systems were used: The closed field unbalanced planar magnetron sputtering system at Colorado School of Mines, powered by a MPP plasma generator power supply, is shown in Fig.4d- left. The planar magnetron system at SWRI, powered by PEMS with an external ion source or by a Huettinger HIPIMS power supply, on loan from the Government, is shown in Fig. 4d-right.

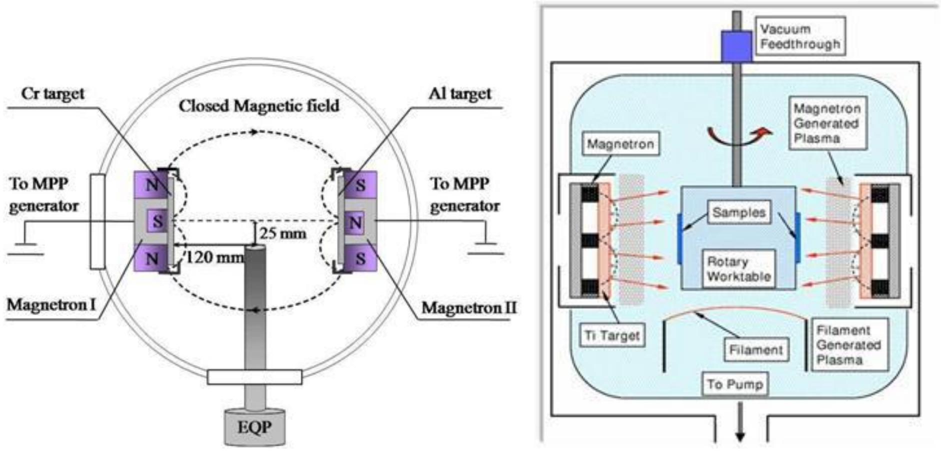
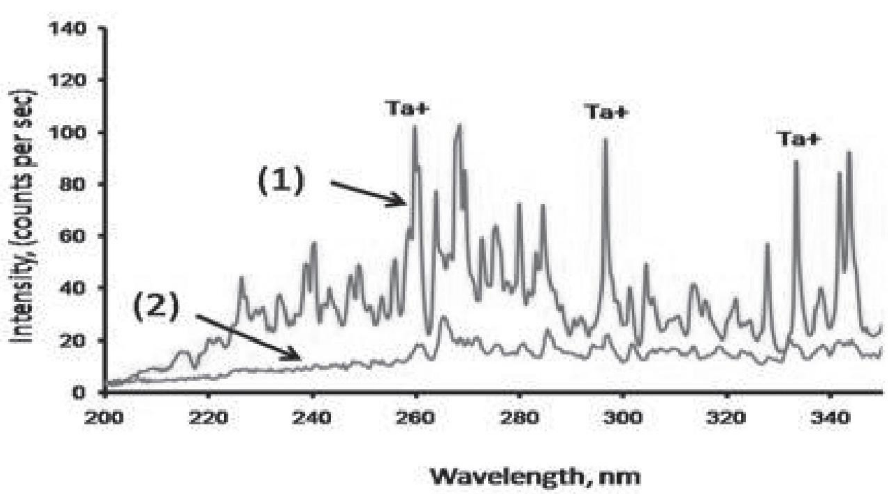


Fig. 4d Schematics of planar magnetron systems used to study Ta and CrN films: Colorado School of Mines unbalanced magnetron sputtering system on the left; SWRI plasma enhanced PEMS system on the right.

5. HIPIMS-MPP Plasma Characterization:

5a) Ta Discharge by Optical Emission Spectrum (OES): A Ta target was used in the study of deposition of Ta coatings. The OES for MPP generated Ta plasma in comparison with conventional DCMS generated plasma is shown in Fig. 5a in two wavelength ranges. The data showed that the intensity of Ta lines was reduced in MPP compared with DCMS generated plasma, but the intensity of Ta + increased in MPP compared with DCMS plasma [8]. The spectra did not show the presence of Ta ions in DCMS discharge (line 2), but MPP sputtering process showed the presence of Ta ions and Ar ions (line 1). The abundant Ta ions in the MPP Ta discharge are used to grow dense quality Ta films using MPP technology; while in DCMS, predominately Ta neutrals are used to grow Ta films [10, 11].



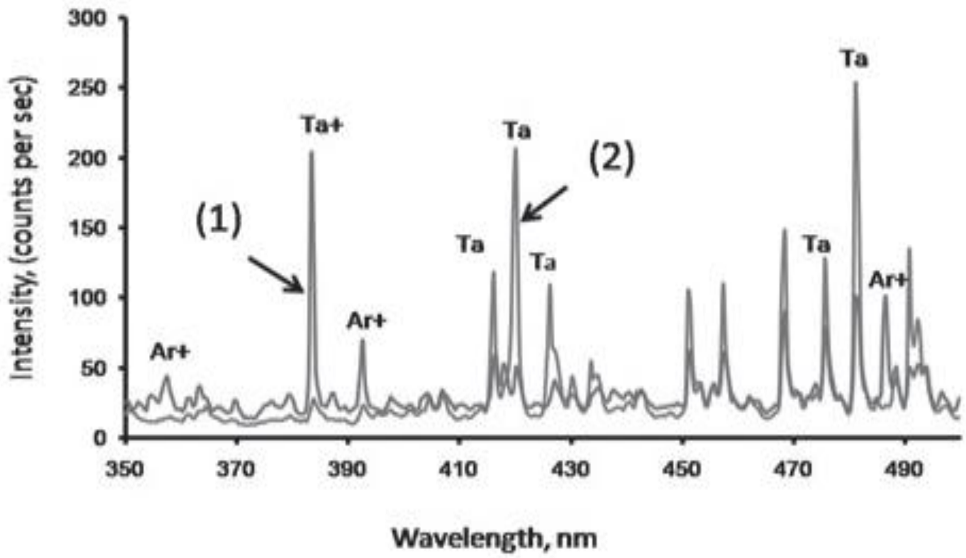


Fig. 5a Comparison of Optical Emission Spectrum (OES) for MPP (Line 1) and conventional DCMS (Line 2) generated plasma in wavelength range: top 200-350 nm; bottom 350-500nm.

5b) HIPIMS-MPP Ta discharge characterized by electrostatic quadrupole plasma mass spectrometer (EQP): To further characterize the ion mass and ion energy distributions of the Ta discharge, a Hiden electrostatic quadrupole plasma mass spectrometer (EQP) was used [12-14]. In Fig. 5b, mass and ion energy distribution for Ta discharge showed the presence of $^{181}Ta^{+}$, $^{181}Ta^{++}$, and $^{40}Ar^{+}$ at various sputtering pressure is shown. The $^{181}Ta+$ ions are the most prevalent species present, exceeding the intensity of the $^{40}Ar^{+}$ ions. The intensity of the ions present in the MPP process is quite different than what is observed during the sputtering of Ta with conventional DCMS. The ions with higher than 1^{+} are responsible for a potential secondary electron emission process that has a higher emission coefficient than the kinetic secondary emission found in conventional glow discharges. The establishment of a potential secondary electron emission may enhance the current of the discharge. The abundant Ta ions are used to grow dense quality Ta films using MPP technology. In DCMS, predominately Ta neutrals are used to grow Ta films.

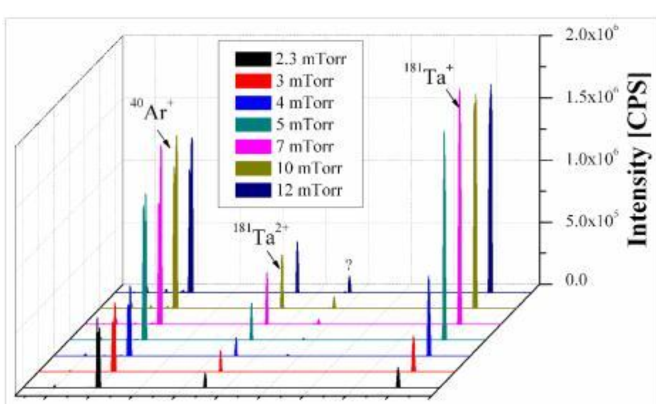


Fig. 5b Ion-mass distributions of HIPIMS-MPP Ta discharge at various sputter pressure

5c) **HIPIMS-MPP Cr Discharge in Argon With and Without Nitrogen Reactive Sputtering Gas using EQP**

A Cr target was used in the deposition of Cr and CrN coatings. In Fig. 8, the EQP data for MPP generated plasma using a Cr target with and with the addition of nitrogen gas to argon sputtering gas is shown [15, 16]. The left figure shows the plasma characteristics using a Cr target for the deposition of Cr coatings; the right shows the addition of N^2 gas to Ar for the deposition of CrN. The plasma consists of singly and doubly charged ^{52}Cr ions and ^{14}N ions. These figures show that Cr target has been ionized. The Cr ions can grow Cr coatings; and they can also combine with nitrogen ions to grow CrN films. In DCMS, predominately Cr neutrals as used to grow Cr and CrN coatings.

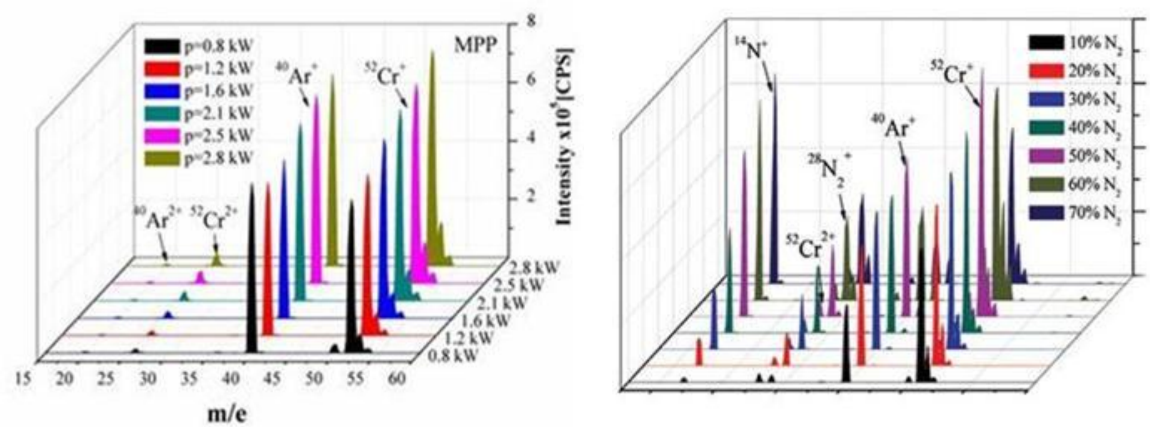


Fig. 5c HIPIMS-MPP discharge using a Cr target: 1) left- with only argon gas; and 2) right- with nitrogen gas in argon, for reactive deposition of CrN coatings.

6. Results for Ta and Cr Depositions:

6a) MPP deposited Ta coatings topography and microstructure:

In this MPP study of Ta depostion, the surface of the samples was cleaned with Radio Frequency (RF) sputter etch process at RF power ~ 200 W, substrate bias -700 V, sputter etch process time ~ 20 min. Metal samples were sputtered at 10 cm distance target to sample. Ar gas flow ~200 sccm or 5 mTorr pressure. Target power density was in the range of 0.37 kW/ cm^2. In Fig. 6a, MPP deposited Ta coating is compared with DCMS deposited Ta films and production electroplated HC Cr coatings. The data showed MPP deposited Ta has dense small grains, featherless microstrucure, small grains, smooth surfaces; while production electroplated Cr has

extensive cracks; and DCMS deposited film has high collumnar mirostructure with porosity, larger grains, more rough surfaces [10]. Porous coatings allowing hot propellent gases to penetrate the coatings is the major cause of high temperature wear and erosion in gun barrels. Porous coatings allowing water vapor or other environmental chemicals to penetrate throught the coatings to expose the substrate is the major cause of corrosion and failure of many ordnance components. These results showed that new dense HIPIMS-MPP coatings can be excellent alteranitves for corrosion and erosion resistance replacing HC Cr, whch contains high porosity.

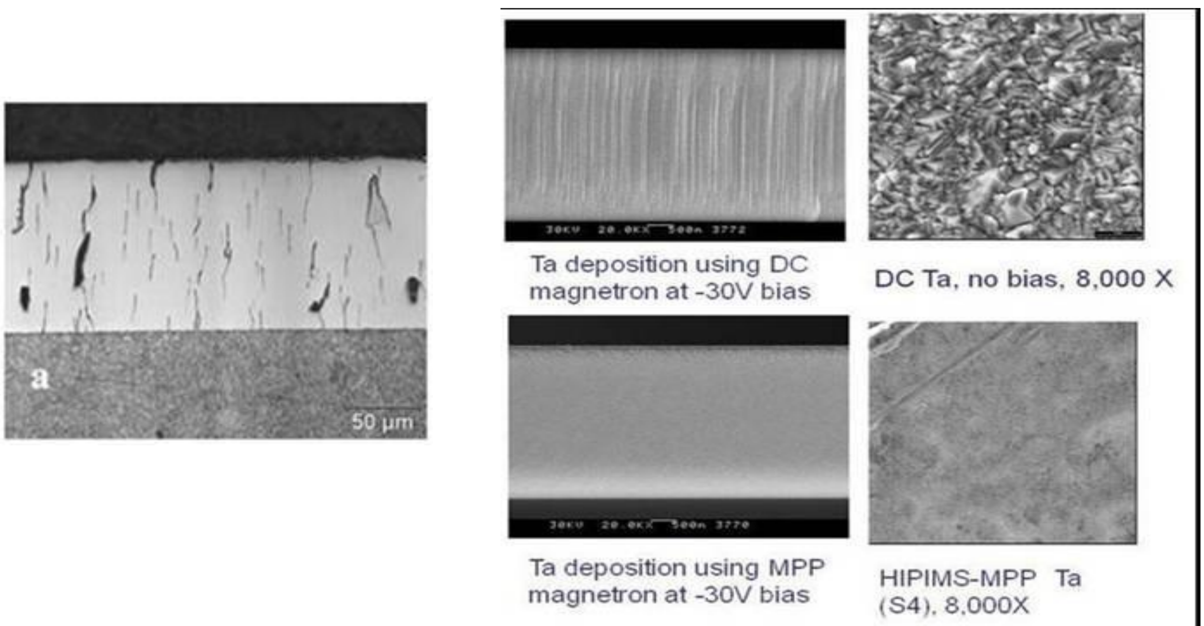


Fig. 6a Morphology comparison of Ta films: Left- Production HC Cr cross section with numerous cracks; 2) Middle- DCMS and HIPIMS-MPP cross section comparison; 3) Right- DCMS and HIPIMS-MPP topography comparison.

6b) MPP Ta coatings depositions at three substrate bias voltages

In Table 1, MPP depositions at three substrate bias voltages are given. The data showed that: 1) Phase dependence on substrate bias voltage at -50 volts; 2) High hardness and residual stress increased as negative biased voltage increased, which is expected due to the higher ion bombardment. In Fig. 6b, XRD results illustrate that sample S1 deposited at bias voltage of -30 volt, Ta was predomiantly tetragonal beta Ta; sample S2 deposited at -40 volt, Ta was a mixutre of bcc and tetragonal; and sample S4, deposited at -50 volt bias voltage, Ta was 100% bcc Ta. In Fig. 6c, S4 topography and microstructure are shown, and topography comparison was made with DCMS depostied Ta coatings. MPP deposited Ta has very dense structure and has very small grains compared to DCMS deposited Ta. The Interface showed minor white tetragonal beta Ta fingers in bcc alpha Ta.

Table 1 MPP depositon of Ta in planar magnetron configuration at various bias

Sample	Deposit Time (min)	Bias Voltage (V)	Pulse Shape	Thick (μm)	Phase	Residual Stress (MPa)	Hardness (HK50)
#S1	180	-30	1	20	β + α	-980 ± 312	
#S2	180	-40	1	17	α + β	-1,382 ± 158	504
#S4	180	-50	1	16	α	-1,516 ± 183	581

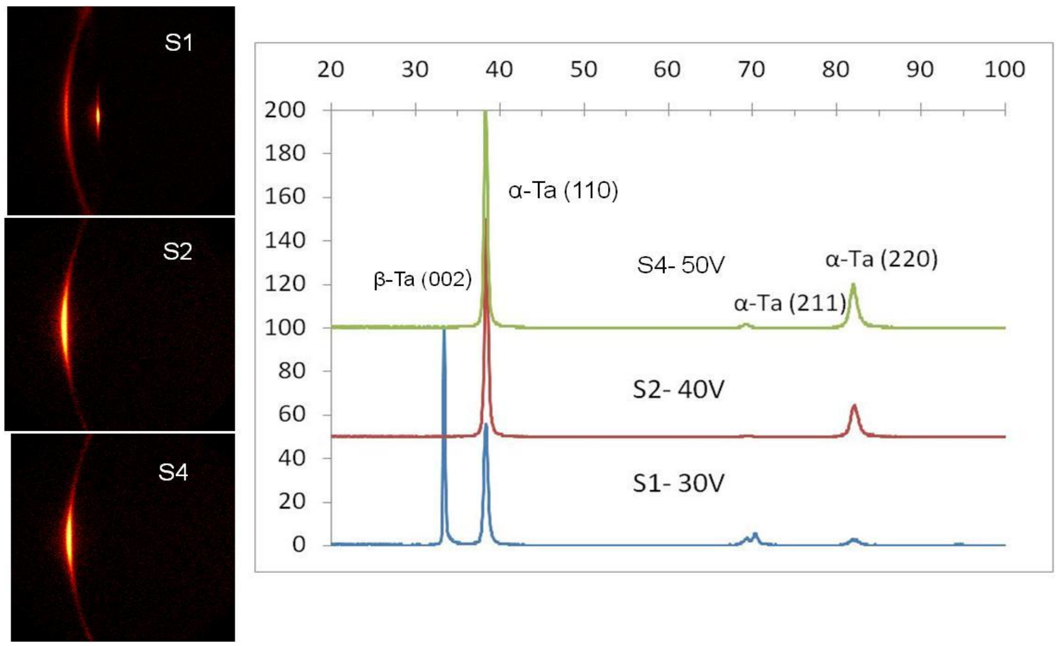


Fig. 6b MPP depostion of Ta in planar geometry: 1) left- 2D XRD using Bruker D8 with area detector; 2) right- XRD using a Scintag PTS diffractometer; showing Ta deposited at -30, -40, -50 volts substrate bias. The results showed strong phase dependence on bias voltage [8].

MPP #S4, 500X MPP #S4, 15,000X DC pulsed, 8,000X

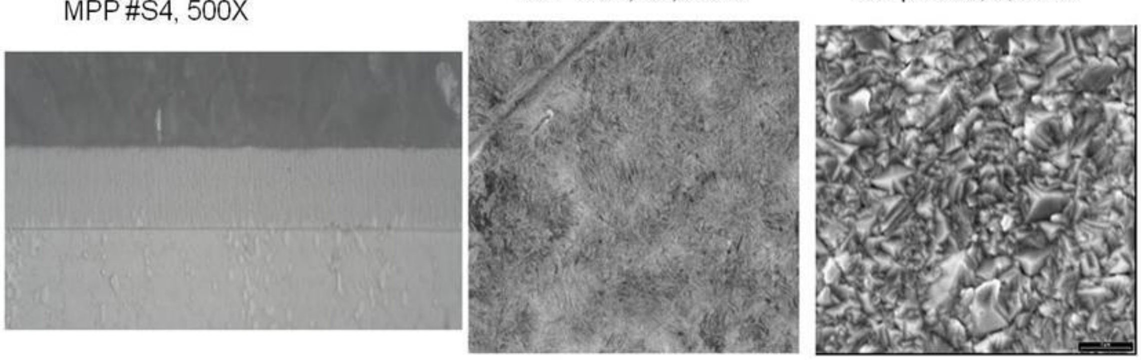


Fig. 6c HIPIMS-MPP Ta sample S4: 1) Left: Microstructure showing less features; 2) Middle: topography showing smoother surfaces; 3) Right: Ta topography at x15,000 magnification compared to previously DCMS deposited Ta film at x8,000 magnification [9].

6c) Parametric study of effect of substrate bias voltage and argon pressure

Due to the critical importance of Ta phase dependence on the substrate bias voltage as noted from the previous section, systematic parametric studies of phase and microstrucutre dependence on substrate bias voltage and sputter pressure were performed [12-14]. The results ares hown in Fig. 6d for bias effect, Fig. 6e for sputter gas pressure effect, Fig. 6f for grain size effect. Data in Fig. 6d demonstrated that low substrate bias voltages below -30 volts resulted in tetragonal beta Ta with (002) preferred orientation. Bias voltage at -40 volts resulted in mixed alpha and beta Ta. At bias voltage above -50 volts, bcc alpha Ta resulted. The cross over voltage from beta to alpha Ta is at ~40-50 volts. Data from Fig. 6e dmonstrated that low sputter gas pressures resulted in bcc alpha Ta, high sputter pressures resulted in tetragonal beta Ta, with cross over at 4-5 mTorr gas pressure; film cross secction showed more columnar microstructure at low gas pressures 2-r mTorr, but featurless microstructure when gas pressures increased from 5-10 mTorr. Data from Fig. 6f showed substrate bias was dense with small grain size compared to floating substrtae bias. Based on this study, MPP depostion of Ta is at -50 volt bias, and 4 mTorr argon pressure is recommended for optimal phase and mcirsotructure properties.

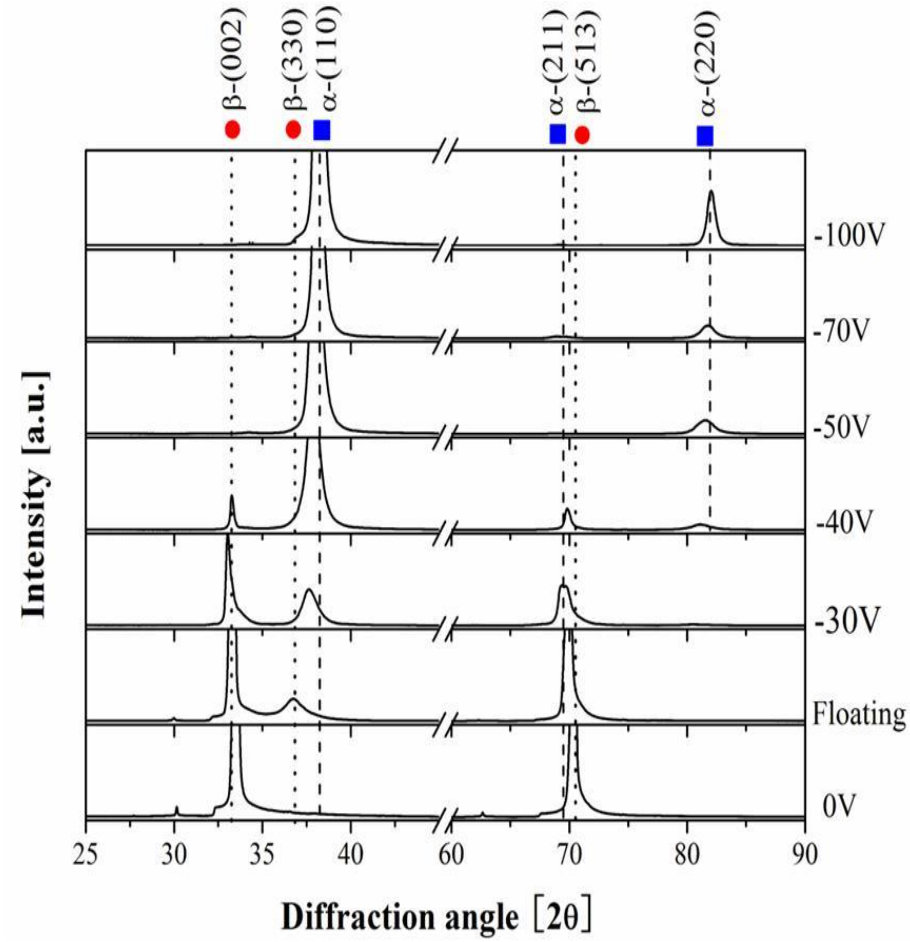


Fig. 6d XRD data showing Ta phase dependence on bias voltage in MPP Ta deposition...

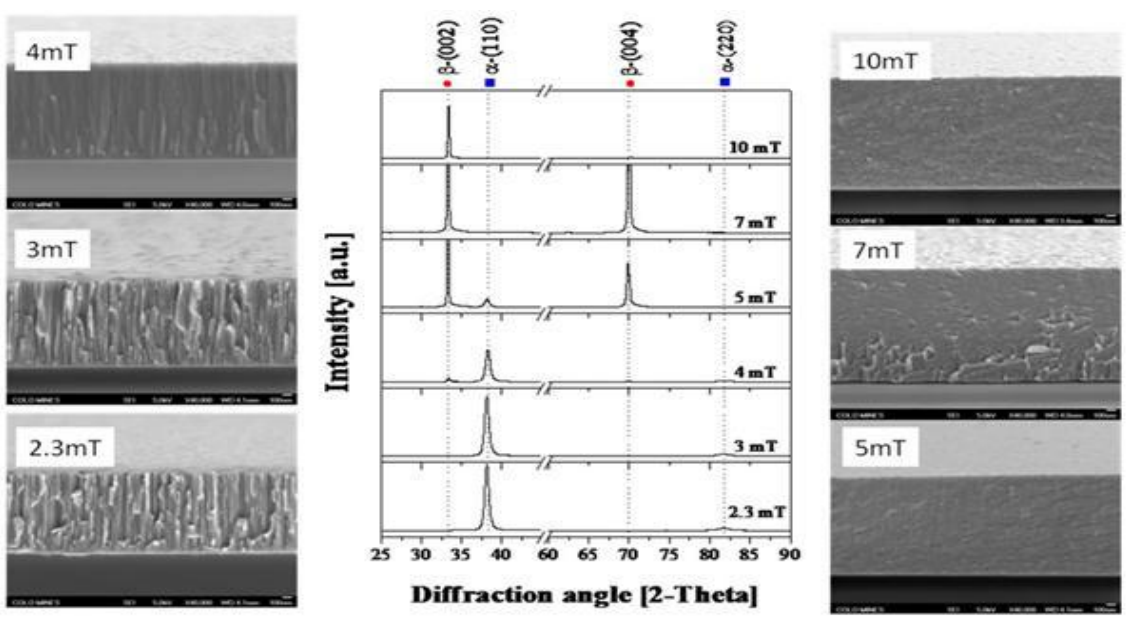


Fig. 6e XRD and SEM data showing Ta phase and microstructure dependence on sputter gas pressure in the MPP deposition of Ta coatings [9-11].

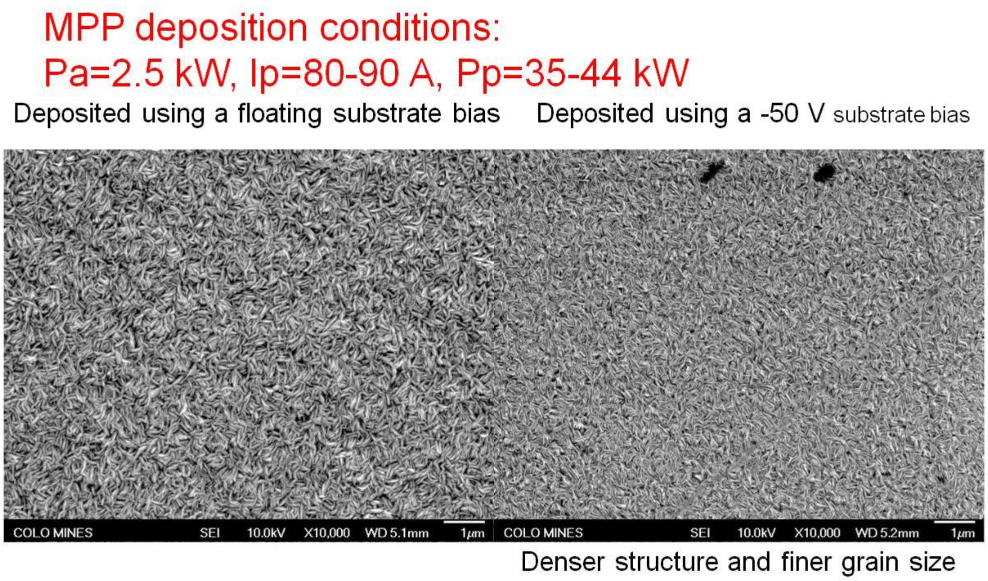


Fig. 6f SEM topography showing effects of biasing on grain size of MPP deposited Ta coatings; left: floating bias; right- -50 volt bias.

6d) MPP deposited thick Ta coatings Pulsed Laser Heating Adhesion Test

MPP deposition technique was used to deposit thick bcc Ta coatings on A723 steel. The sample was subjected to pulse laser heating (PLH) test at 2.5 msec, 1.0 J/mm2, 20 cycles, simulating ~1400ºC temperature. Fig. 6g shows the pulsed laser heating test results of 90µm thick Ta samples deposited on A723 gun steel, compared to a 125µm electroplated HC Cr deposited on A723 steel under the same PLH conditions. While HC Cr is full of cracks causing erosion of the substrate steel, the MPP Ta coated steel showed excellent alpha Ta phase, excellent adhesion, no cracking, and no delamination. Fig. 6h shows the hardness measurement and expanded view of the bcc Ta coating. The thin white interface layer was attributed to the tetragonal beta Ta coatings, which converted to bcc alpha Ta coatings under pulsed laser heating. Hardness measurements were made in the corresponding coatings, steel, and interface areas; showing interface area is much harder. The HAZ (Heat affected zone) that developed in the Ta/Steel interface is a result of the transformation of tempered martensite to untempered martensite resulting from temperatures into austenite region.

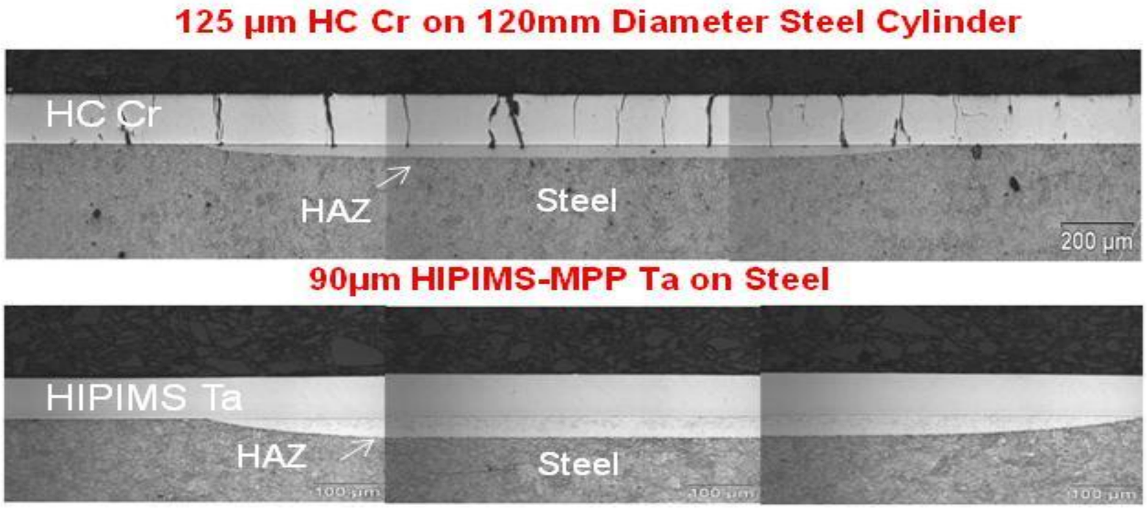


Fig. 6g Pulsed Laser Heating (PLH) adhesion test of MPP deposited Ta coatings compared to HC Cr deposited on A723 steel. MPP showed no cracks and no delamination, as HC Cr showed extensive cracks. HAZ indicted heat affected zone in steel due to tempered to untempered martensite transformation.

PL-Ta Mines 2-01

Diamond Length (µ)	Knoop (Hk_{50})	Depth of Diamond (µ)	
36.64	530	-98.35	
37.57	505	-79.34	-Steel
39.68	451	-62.38	
29.54	815	-31.43	
30.75	752	-16.72	- HAZ
29.84	823	-6.63	
35.33	569	12.15	
34.52	598	28.53	
33.10	649	46.51	- Ta
33.10	649	61.02	
33.82	623	75.43	

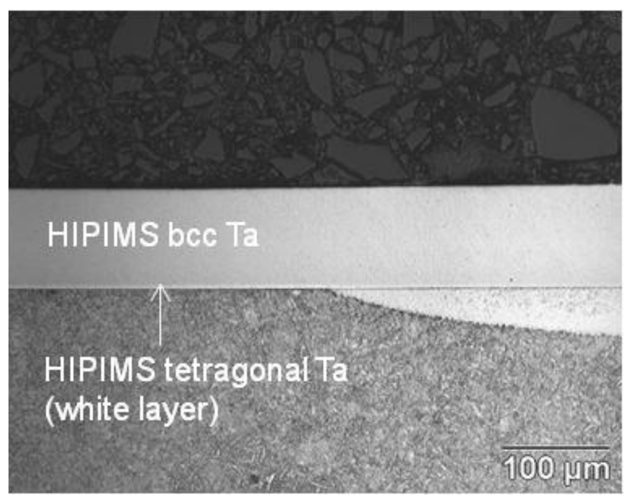


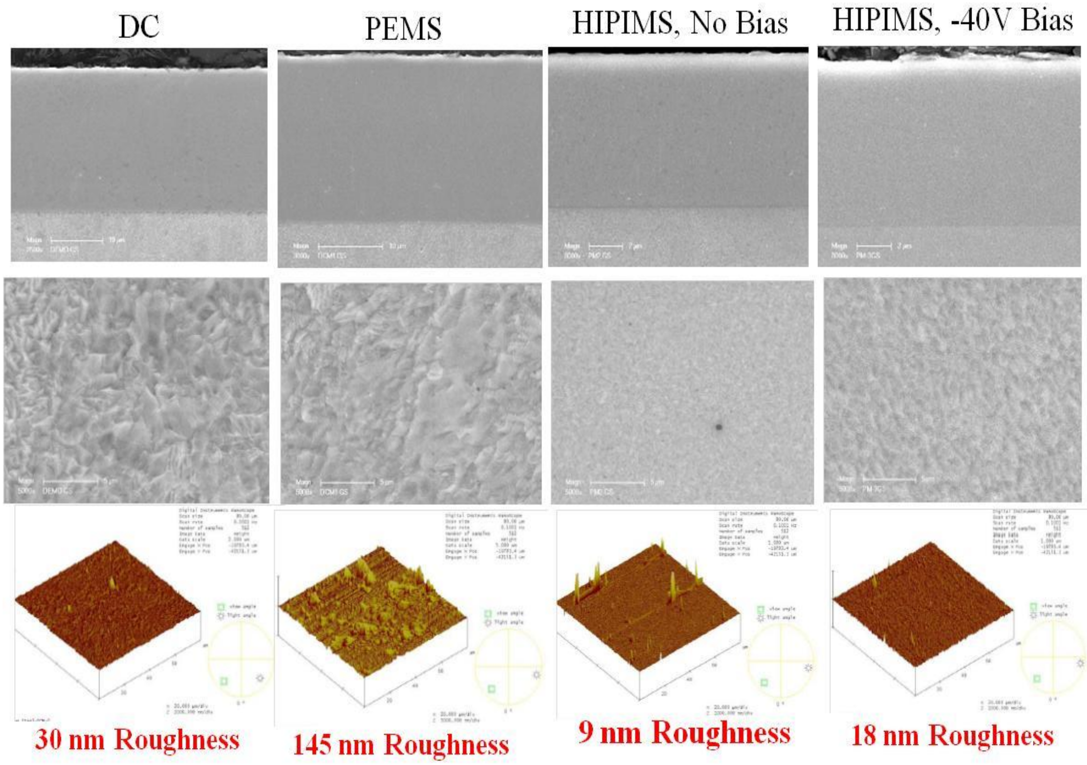
Fig. 6h MPP deposited 90µm Ta on A723 steel: 1) left- Harness measurements; 2) right- pulsed laser heating test showing dense adhesive crack-resistant predominately alpha Ta coatings with interface tetragonal beta Ta.

6e) **Comparison of Planar Magnetron DCMS, PEMS, HIPIMS Depositions**

DCMS is a common PVD coating deposition technique. It was also the technology used in Benet's cylindrical magnetron sputtering programs to coat 120mm bore surfaces. It is important to compare DCMS, PEMS, and HIPIMS, in this section. As shown in Table 2, the average power for the three sputtering techniques was set at 2 kW and the deposition was conducted in an Ar atmosphere, and the deposition was one hour. After the depositions, SEM, XRD, AFM, microhardness, RC indentation, and scratch tests were performed to study the coatings properties. In Fig. 6i, DC, PEMS, and HIPIMS are compared. It was observed that from Table 2 and Fig. 6i that: 1) The deposition rates for the DCMS and PEMS are comparable; 2) DCMS deposition rate is higher than HIPIMS; 3) RC indentation tests showed that adhesion of the DCMS sputtered film is not as strong as those of the PEMS and HIPIMS deposited films; 4) The surface roughness measured by AFM showed that HIPIMS deposited films is lower than all other ones prepared by PEMS and DCMS; 5) The hardness for HIPIMS films are higher, expected due to the higher ion bombardment.

Table 2 Comparison of DCMS, PEMS, HIPIMS deposition of Cr

Sample No.	Sputter Deposition Mode	I disch (A)	V bias (V)	Deposit Time (h)	Film Thick-ness (μm)	Surface Rough-ness (nm)	Hv 25g (kgf/mm^2)
DCM0	Conventional magnetron	-	-100	1	23.5	30.0	211.2
DCM1	PEMS	5	-40	1	23.2	145.4	235.4
PM2	HIPIMS, samples grounded	-	0	1	8.1	8.6	533.4
PM3	HIPIMS, samples biased	-	-40	1	8.7	18.2	317.2
PM4	HIPIMS with enhanced plasma	10	-40	1	11.3	32.5	248.2



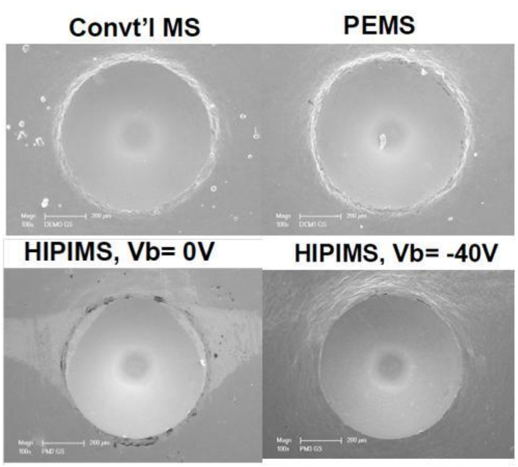


Fig. 6i Comparative Cr deposition using DCMS, PEMS, HIPIMS: Upper: Row 1- cross section, Row 2- topography, Row 3- AFM surface roughness. Left- RC indentation testing showing conventional DCMS deposited Cr has poor adhesion compared to PEMS and HIPIMS with and without bias.

6f) MPP coated bcc Ta film using plasma enhanced cylindrical magnetron at Benet

Benet deposited a 106µm thick bcc Ta film on a 120mm bore sample with the substrate ground at a high 20 mTorr sputtering pressure. Fig. 6j shows the dense microstructure and moderate hardness in the bcc Ta coatings. The white tetragonal beta Ta fingers were observed in the darker bcc alpha Ta lattice in the SEM microstructure image. At substrate ground, the coatings were expected to be beta Ta at 5 mTorr argon.. Fig. 6k shows the result of pulsed laser heating adhesion test at 2.5 msec, 1.0 J/mm2, 20 cycles, simulating ~1400ºC temperature of Ta versus HC Cr under the same conditions. Pulsed laser heating test showed no HAZ, no cracking, no

delamination. The results showed that successful adhesive, thick, dense, bcc phase alpha Ta, can be deposited on A723 steel using new HIPIMS-MPP technology. However, further experiments should be performed using lower argon pressure, since argon pressure can affect coatings density. There was no explanation why there was no heat affected zone in steel was observed.

Z2-2

Diamond Length (µ)	Knoop (Hk_{50})	Depth of Diamond (µ)
46.86	326	5.67
47.18	319	25.78
47.51	315	45.53
47.32	318	64.51
48.96	297	82.74

Fig. 6j Benet deposited bcc alpha Ta coatings using a MPP plasma enhanced cylindrical magnetron system showing dense coatings and moderate hardness giving good ductility.

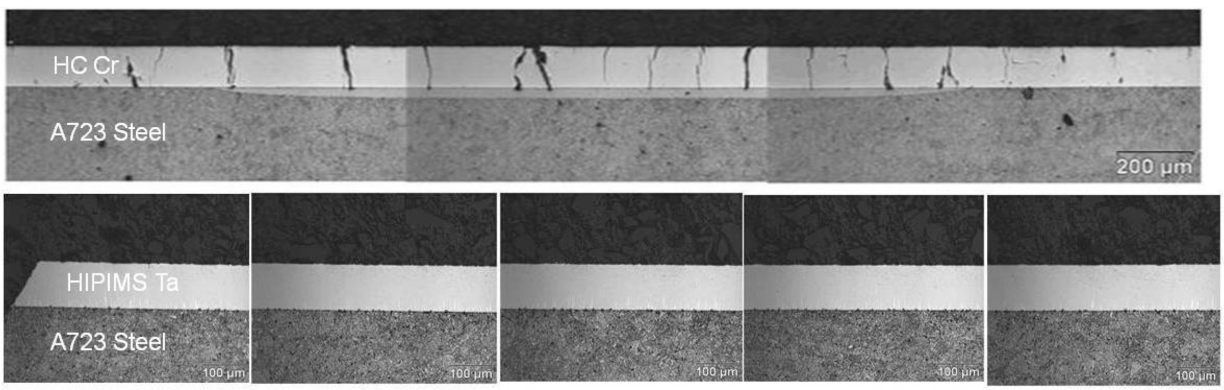


Fig. 6k Benet deposited bcc alpha Ta coatings using a MPP plasma enhanced cylindrical magnetron system: 1) Top- pulsed laser heating of HC Cr coatings; 2) Bottom- pulsed laser heating of MPP Ta under the same test conditions, showing no cracking, no delamination, no heat affected zone.

7. Results of CrN Depositions

7a) Topography and Microstructure of CrN films

CrN is being studied to protect ordnance against wear, corrosion, erosion. The application to ordnance such as the 155mm breech-spindle calls for coatings ~10µm in thickness. In this work, CrN coatings of 10-55µm thick are being studied using DCMS, PEMS, HIIMS-MPP processes on test 4340 steel and 1020 steel test sheets of 3 inch x 6 inches [15, 16]. Fig. 7a shows 1020 steel

samples coated with, from left to right, 0, 8, 10, 20 µm HIPIMS-MPP CrN coatings. When coating thickness increased, compressive residual stresses increased. The specimen on the extreme right with 20 µm CrN coatings deposited on it had the highest curvature. Curvature is not expected when coating is applied on thicker substrates. Fig. 7b shows the microstructure of HIPIMS-MPP CrN depositions on steel showing very dense and adhesive coatings, with no cracking, no delamination. Comparison is made in Fig. 7b with HC Cr, which has high porosity; and DCMS deposited CrN with high columnar microstructure and high porosity.

Fig. 7a CrN coatings deposited on test 1020 steel samples, from left to right: 0, 8, 10, 20 µm CrN on 1020 steel [14].

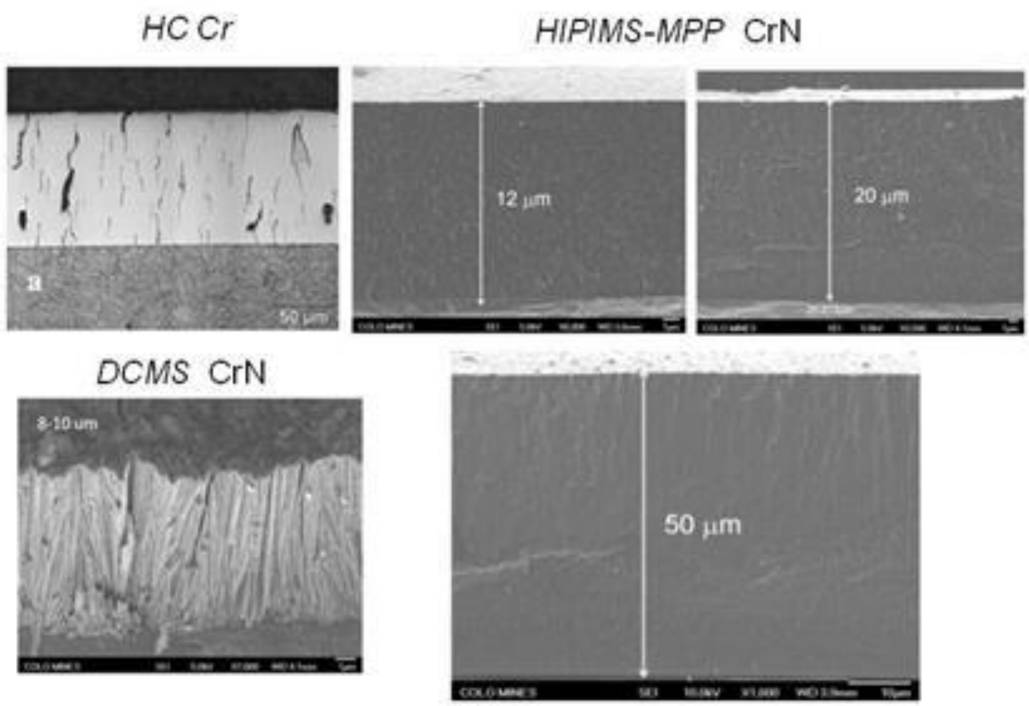


Fig.7b Comparison of HC Cr, DCMS, HIPIMS-MPP deposited CrN: HIPIMS-MPP deposited CrN has very dense microstructure, while HC Cr and DCMS deposited CrN coatings have high porosity.

7c) **Corrosion testing of HIPIMS-MPP and PEMS deposited CrN Films**

Corrosion tests were performed made using a Gamry corrosion tester and artificial sea water of PEMS and HIPIMS deposited CrN samples [16]. Comparative corrosion test results for CrN and HC Cr coatings of comparative thickness are shown in Fig. 7c. References to the corrosion test using Gamry corrosion tester on ASEM tests are: 1) ASTM D1141-98 "Standard Practice for the Preparation of Substitute Ocean Water"; 2) ASTM G3-89 "Standard Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing", and 3) ASTM G5-94 "Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements" . Corrosion test results showed that HIPIMS CrN has the best corrosion resistant performance due to the higher density; PEMS CrN has the next corrosion resistant performance. Both are superior to the test sample with electroplated HC Cr coatings.

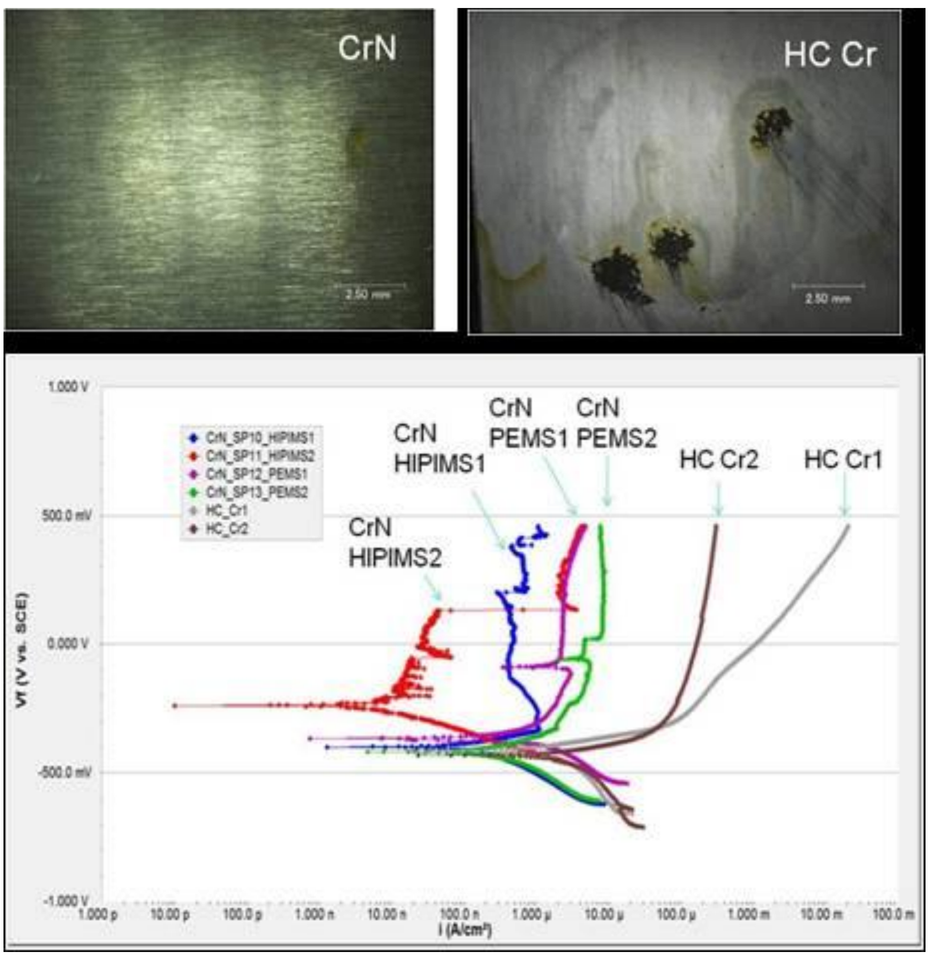


Fig. 7c Corrosion testing of CrN coatings deposited using PEMS and HIPIMS in comparison with production HC Cr coatings; showing superior performance of PEMS and HIPIMS coatings compared to HC Cr for corrosion resistance.

D. Discussion

1) The greatest innovation of the HIPIMS technology is coatings densification, improved morphology, and reduced porosity. In PEMS technology, higher ionization and more intense plasma with added substrate biasing allow the growth of very dense and adhesive films. HIPIMS-MPP technology has the added advantage of higher ionization and ionization of the target metal species. The high flux metal ions of Ta and Cr are used to grow hard dense quality coatings. HIPIMS technology can grow coatings of zone 2 and 3 microstructure with equiaxed structure in Thorton's microstructure zone diagram, at low deposition temperatures. The quiaxed grain structure can enhance the mechanical properties and other properties of the films.

2) HIPIMS technology with high concentrations of metal ions can improve coatings topography, microstructure, and film coverage. This is due to plasma ion interactions with surfaces. The motion of neutral atoms is difficult to control, but ions can be collimated by an electric field, and ion bombardment energy can be controlled by applying a bias voltage to the substrate. In HIPIMS-MPP depositions, ion-surface interaction improves film microstructure and coverage.

3) Increased ion bombardment through increased ionization and biasing can improve film properties, but it can also increase residual stresses. In thin films, this is not a problem. However, in thick coatings, high residual stresses can cause delamination and poor adhesion, if not properly managed. High ion intensity, low energetic ions are recommended.

4) Crystalline phase control is critical in Ta deposition. As shown in this work, alpha and beta Ta films can be formed depending on substrate bias and gas pressure. Proper control of the energetic in HIPIMS-MPP depositions is recommended to deposit bcc alpha Ta.

E. Conclusions

1. PVD PEMS technology generated improved plasma intensity and current density to increase ion bombardment; HIPIMS and MPP generated high intensity high ionization metal plasma.
2. PEMS, HIPIMS, MPP technologies deposited dense coating with less columnar microstructure; superior to DCMS deposited coatings and to production HC Cr coatings with porosity for ordnance protection.
3. New technology successfully deposited Ta 100-150 µm on steel for future 120mm and 155mm applications. The coatings were dense, bcc alpha Ta, with excellent ductility, microstructure, adhesion, and high temperature properties.

4. Ta phase is sensitive to deposition parameters, such as substrate bias and sputter gas pressure.
5. New technology successfully deposited 10-55 μm fcc CrN coatings on steel. New thick PVD CrN demonstrated dense coatings, good microstructure, and superior corrosion resistance properties compared to electroplated HC Cr.
6. New technology can deposit environmental-friendly coatings, Ta & CrN, for potential replacement of production HC Cr coatings for ordnance applications.

Acknowledgement:

We thank EQBRD for providing funding for the two year R&D work to bring in new coatings technologies into Army R&D. We thank Colorado School of Mines for their contribution in providing coated samples, even though no funding was provided to them under EQBRD.

References:

1. A.P. Ehiasarian, R. New, W.-D. Münz, L. Hultman, U. Helmersson, and V. Kouznetsov, Vacuum 65 (2002) 147.
2. S.L. Lee, R. Wei, "Effects of Increased Ion Bombardment on Magnetron Sputtered Ta and Cr," Soc. for Vac. Coaters, Tech Conf, (2007), 189-195.
3. S.L. Lee and R. Wei, "Plasma-Enhanced Magnetron Techniques for Durable Pollution-Free Large Cal Armament Applications," NDIA Gun and Missile Conference Proceeding, (2008) http://www.dtic.mil/ndia/2008gun_missile/ 6332LeeSabrina.pdf.
4. V. Kouznetsov, K. Macák, J. M. Schneider, U. Helmersson, and I. Petrov, "A Novel Pulsed Magnetron Sputter Technique Utilizing Very High Target Power Densities," Surf. Coat. Technol. 122 (1999) 290.
5. K. Macák, V. Kouznetsov, J. Schneider, U. Helmersson, and I. Petrov, J. Vac. Sci. Technol. A 18(4), 1533 (2000).
6. Ulf Helmersson, M. Lattermann, John Borhmark, Arutiun P. Ehiasarian, Jon T. Gudmundsson, "Review of Ionized PVD technology and applications', Thin Solid Films, Thin Solid Films 513 (2006) 1-24.
7. R. Chistyakov, B. Abraham, W. Sproul, J. Moore, and J. Lin, SVC 50th Annual Tech Conf Proc. (2007) 139.
8. S.L. Lee, M. Doxbeck, J. Mueller, M. Cipollo, P. Cote, "Texture, Structure, and Phase Transformation in Sputtered Beta Ta Coating', Surface and Coatings Tech. 177-178 (2004), 44-51.
9. D. Glocker, Isoflux, ex-Benet contractor, private communication.
10. S.L. Lee, M. Todaro, S. Smith, R. Wei, K. Coulter, "Plasma-enhanced sputtered thick Ta for barrel applications," SVC 52nd Tech Conf. Proc., pp. 558-563, (2009).

11. S.L. Lee, M. Cipollo, F. Yee, R. Chistyakov, B. Abraham, “HIPIMS-MPP sputtered Ta films using I-PVD technology,” SVC 52nd Tech Conf. Proc., pp. 44-49, (2009).
12. S.L. Lee, J. Lin, R. Wei, W. Sproul, J.J. Moore, “Deposition of Environmental Friendly Tantalum and Chromium Nitride Coatings Using HIPIMS-MPP-PEMS Technologies”, SVC 53rd Tech. Conf. Proc. PP125-133, (2010).
13. J. Lin, J. J Moore, W.D. Sproul, Sabrina Lee, Jun Wang, ”Effect of negative substrate bias on the structure and properties of Ta coatings deposited using modulated pulse power magnetron sputtering,” IEEE Transactions on Plasma Science, Vol 38, No. 11, 3071-3078, Nov (2010).
14. William. D. Sproul, Jianliang. Lin, John. J. Moore, Sabrina Lee, Jun Wang, “MPP Deposition of Thick Tantalum Coatings,” SVC 53rd Tech Conf. Proc., pp. 187-192 (2010).
15. Jianliang Lin, William D. Sproul, John J. Moore, Sabrina Lee, Sterling Myers, “High rate deposition of thick CrN and Cr2N coatings using modulated pulse power magnetron sputtering,” Surface and Coatings Tech. 205 pp. 3226–3234 (2011)
16. S.L. Lee and Daniel Schmidt , NDIA Gun and Missile Conference paper, “New PVD Technologies for New Ordnance Coatings”, Miami, FL, Aug 29-Sept 1, (2011). http://www.dtic.mil/ndia/2011gunmissile/Wednesday11583_Lee.pdf